

We claim:

1. A process for producing a higher molecular weight ketone, comprising:

feeding an aldol catalyst solution, a lower molecular weight aldehyde, and a lower molecular weight ketone, through a reactor provided with a solid hydrogenation catalyst and hydrogen gas;

recovering a liquid reactor effluent containing the higher molecular weight ketone as a reaction product; and

recycling a portion of the recovered liquid reactor effluent back through the reactor.

2. The process according to claim 1, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled, of at least about 1 to 1.

3. The process according to claim 1, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled, from about 1 to 1 to about 1000 to 1.

4. The process according to claim 1, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled, from about 1 to 1 to about 100 to 1.

5. The process according to claim 1, comprising a further step of feeding into a second reactor the portion of the liquid reactor effluent that is not recycled.

6. The process according to claim 5, wherein the second reactor is provided with a solid hydrogenation catalyst and hydrogen gas.

5 7. The process according to claim 6, comprising a further step of recycling a portion of a liquid reactor effluent exiting the second reactor back through the second reactor.

10 8. The process according to claim 7, wherein the recycling of a portion of the liquid reactor effluent exiting the second reactor back through the second reactor is carried out at a recycle ratio of the volume of the liquid reactor effluent recycled back through the second reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled back through the second reactor, of at least about 1 to 1.

15 9. The process according to claim 1, wherein the aldol catalyst solution comprises a solution of an alkali- or an alkaline- earth metal hydroxide or alkoxide, wherein the hydroxide or alkoxide is present in the solution in an amount of from about 0.5 to about 50 wt.%.

20 10. The process according to claim 1, wherein the aldol catalyst solution comprises a solution of an alkali- or an alkaline- earth metal hydroxide or alkoxide, wherein the hydroxide or alkoxide is present in the solution in an amount of from about 2 to about 10 wt.%.

25 11. The process according to claim 1, wherein the molar ratio of the hydroxide or alkoxide of the alkali metal or alkaline earth metal catalyst to the lower molecular weight aldehyde is from about 0.001:1 to about 0.4:1.

12. The process according to claim 5, wherein the molar ratio of the hydroxide or alkoxide of the alkali metal or alkaline earth metal catalyst to the lower molecular weight aldehyde is from about 0.05:1 to about 0.15:1.

5 13. The process according to claim 1, wherein the aldol catalyst solution comprises one or more of: sodium hydroxide, potassium hydroxide, cesium hydroxide, lithium hydroxide, magnesium hydroxide, calcium hydroxide, barium hydroxide, sodium methoxide, sodium ethoxide, sodium propoxide, sodium butoxide, potassium methoxide, potassium ethoxide,
10 potassium propoxide, potassium butoxide, cesium methoxide, cesium ethoxide, cesium propoxide, cesium butoxide, lithium methoxide, lithium ethoxide, lithium propoxide, lithium butoxide, magnesium methoxide, magnesium ethoxide, magnesium propoxide, magnesium butoxide, calcium methoxide, calcium ethoxide, calcium propoxide, calcium butoxide, barium
15 methoxide, barium ethoxide, barium propoxide, or barium butoxide.

 14. The process according to claim 1, wherein the aldol catalyst solution comprises one or more of: sodium hydroxide or potassium
20 hydroxide.

 15. The process according to claim 1, wherein the temperature in the reactor is from about 0°C to about 200°C.

 16. The process according to claim 1, wherein the temperature in the
25 reactor is from about 25°C to about 175°C.

17. The process according to claim 1, wherein the temperature in the reactor is from about 90°C to about 130°C.

5 18. The process according to claim 1, wherein the hydrogen gas is provided at a pressure from about 3 to about 150 bar.

19. The process according to claim 1, wherein the hydrogen gas is provided at a pressure from about 15 to about 30 bar.

10 20. The process according to claim 1, wherein the residence time of the reaction mixture in the reactor is from about 2 to about 200 minutes.

21. The process according to claim 1, wherein the residence time of the reaction mixture in the reactor is from about 10 to about 60 minutes.

15 22. The process according to claim 1, wherein the recycle ratio is from about 5:1 to about 30:1.

20 23. The process according to claim 1, where the hydrogenation catalyst is a shaped or extruded transition metal catalyst supported on a stable support.

24. The process according to claim 1, wherein the hydrogenation catalyst comprises one or more of: Ni, Co, Cu, Cr, Pt, Pd, Rh, Ru, Re, or Ir.

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25. The process according to claim 1, wherein the hydrogenation catalyst is supported on a stable support comprising one or more of: alumina, silica, silica-alumina, or carbon.

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26. The process according to claim 1, wherein the hydrogenation catalyst comprises palladium on carbon.

10 27. The process according to claim 1, wherein the hydrogenation catalyst has a metal loading of from about 0.1 to about 90 wt.%.

28. The process according to claim 1, wherein the hydrogenation catalyst has a metal loading of from about 0.1 to about 5 wt.%.

15 29. The process according to claim 1, wherein the lower molecular weight aldehyde comprises one or more of: acetaldehyde; propionaldehyde; n-butyraldehyde; 2-methyl-propanal; n-pentanal and structural isomers such as 2-methyl-butanal, 3-methyl-butanal, 2,2-dimethyl-propanal; n-hexanal and structural isomers such as 2-ethyl-butanal, 2,2-dimethylbutanal, 2,3-
20 dimethylbutanal, 2-methyl-pentanal, 3-methylpentanal, 4-methyl-pentanal; n-heptanal and structural isomers such as 2-methylhexanal, 2-ethylpentanal, 2,2-dimethylpentanal, 2,3-dimethylpentanal, 2,4-dimethylpentanal, 2-ethyl-3-methylbutanal, 2-ethyl-2-methylbutanal; n-octanal and structural isomers such as 2-ethylhexanal, n-nonanal and
25 structural isomers; cyclopropane carboxaldehyde; cyclobutane carboxaldehyde; cyclopentane carboxaldehyde; cyclohexane

carboxaldehyde; 2-methylcyclohexane carboxaldehyde; 3-methylhexane carboxaldehyde; and 4-methylhexane carboxaldehyde

5 30. The process according to claim 1, wherein the lower molecular weight ketone comprises one or more of: acetone, 2-butanone, 2-pentanone, and 3-methyl-2-butanone.

 31. A process for producing methyl amyl ketone, comprising:
 feeding an aldol catalyst solution, n-butyraldehyde, and acetone,
10 through a reactor provided with a solid hydrogenation catalyst and hydrogen gas;
 recovering a liquid reactor effluent containing methyl amyl ketone as a reaction product; and
 recycling a portion of the recovered liquid reactor effluent back
15 through the reactor.

 32. The process according to claim 31, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the
20 liquid reactor effluent that is not recycled, of at least about 1 to 1.

 33. The process according to claim 31, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the
25 liquid reactor effluent that is not recycled, from about 1 to 1 to about 1000 to 1.

34. The process according to claim 31, comprising a further step of feeding into a second reactor the portion of the liquid reactor effluent that is not recycled.

5 35. The process according to claim 29, wherein the second reactor is provided with a solid hydrogenation catalyst and hydrogen gas.

10 36. The process according to claim 35, comprising a further step of recycling a portion of a liquid reactor effluent exiting the second reactor back through the second reactor, at a recycle ratio of the volume of the liquid reactor effluent recycled back through the second reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled back through the second reactor, of at least about 1 to 1.

15 37. The process according to claim 31, wherein the aldol catalyst solution comprises a solution of an alkali- or an alkaline- earth metal hydroxide or alkoxide, wherein the hydroxide or alkoxide is present in the solution in an amount of from about 0.5 to about 50 wt.%.

20 38. The process according to claim 31, wherein the molar ratio of the hydroxide or alkoxide of the alkali metal or alkaline earth metal catalyst to n-butyraldehyde is from about 0.001:1 to about 0.4:1.

25 39. The process according to claim 31, wherein the aldol catalyst solution comprises one or more of: sodium hydroxide or potassium hydroxide.

40. The process according to claim 31, wherein the temperature in the reactor is from about 0°C to about 200°C.

41. The process according to claim 31, wherein the hydrogen gas is provided at a pressure from about 3 to about 150 bar.

5 42. The process according to claim 31, wherein the residence time of the reaction mixture in the reactor is from about 2 to about 200 minutes.

10 43. The process according to claim 32, wherein the recycle ratio is from about 1:1 to about 1000:1.

15 44. The process according to claim 31, where the hydrogenation catalyst is a shaped or extruded transition metal catalyst supported on a stable support.

 45. The process according to claim 31, wherein the hydrogenation catalyst comprises one or more of: Ni, Co, Cu, Cr, Pt, Pd, Rh, Ru, Re, or Ir.

20 46. The process according to claim 31, wherein the hydrogenation catalyst is supported on a stable support comprising one or more of: alumina, silica, silica-alumina, or carbon.

 47. The process according to claim 31, wherein the hydrogenation catalyst comprises palladium on carbon.

48. A process for producing methyl isoamyl ketone, comprising:
feeding an aldol catalyst solution, i-butyraldehyde, and acetone, through a
reactor provided with a solid hydrogenation catalyst and hydrogen gas;

5 recovering a liquid reactor effluent containing methyl isoamyl ketone
as a reaction product; and

recycling a portion of the recovered liquid reactor effluent back
through the reactor.

10 49. The process according to claim 48, wherein the recycling is
carried out at a recycle ratio of the volume of liquid reactor effluent recycled
back through the reactor, with respect to the volume of the portion of the
liquid reactor effluent that is not recycled, of at least about 1 to 1.

15 50. The process according to claim 48, wherein the recycling is
carried out at a recycle ratio of the volume of liquid reactor effluent recycled
back through the reactor, with respect to the volume of the portion of the
liquid reactor effluent that is not recycled, from about 1 to 1 to about 1000
to 1.

20 51. The process according to claim 48, comprising a further step of
feeding into a second reactor the portion of the liquid reactor effluent that is
not recycled.

25 52. The process according to claim 51, wherein the second reactor
is provided with a solid hydrogenation catalyst and hydrogen gas.

53. The process according to claim 52, comprising a further step of
recycling a portion of a liquid reactor effluent exiting the second reactor
30 back through the second reactor, at a recycle ratio of the volume of the

liquid reactor effluent recycled back through the second reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled back through the second reactor, of at least about 1 to 1.

5 54. The process according to claim 48, wherein the aldol catalyst solution comprises a solution of an alkali- or an alkaline- earth metal hydroxide or alkoxide, wherein the hydroxide or alkoxide is present in the solution in an amount of from about 0.5 to about 50 wt.%.

10 55. The process according to claim 48, wherein the molar ratio of the hydroxide or alkoxide of the alkali metal or alkaline earth metal catalyst to the i-butyraldehyde is from about 0.001:1 to about 0.4:1.

15 56. The process according to claim 48, wherein the aldol catalyst solution comprises one or more of: sodium hydroxide or potassium hydroxide.

 57. The process according to claim 48, wherein the temperature in the reactor is from about 0°C to about 200°C.

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 58. The process according to claim 48, wherein the hydrogen gas is provided at a pressure from about 3 to about 150 bar.

25 59. The process according to claim 48, wherein the residence time of the reaction mixture in the reactor is from about 2 to about 200 minutes.

60. The process according to claim 49, wherein the recycle ratio is from about 1:1 to about 1000:1.

5 61. The process according to claim 48, where the hydrogenation catalyst is a shaped or extruded transition metal catalyst supported on a stable support.

10 62. The process according to claim 48, wherein the hydrogenation catalyst comprises one or more of: Ni, Co, Cu, Cr, Pt, Pd, Rh, Ru, Re, or Ir.

15 63. The process according to claim 48, wherein the hydrogenation catalyst is supported on a stable support comprising one or more of: alumina, silica, silica-alumina, or carbon.

 64. The process according to claim 48, wherein the hydrogenation catalyst comprises palladium on carbon.

20 65. A process for producing methyl propyl ketone, comprising:
 feeding an aldol catalyst solution, acetaldehyde, and acetone, through a reactor provided with a solid hydrogenation catalyst and hydrogen gas;
 recovering a liquid reactor effluent containing methyl propyl ketone as a reaction product; and
25 recycling a portion of the recovered liquid reactor effluent back through the reactor.

66. The process according to claim 65, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled, of at least about 1 to 1.

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67. The process according to claim 65, wherein the recycling is carried out at a recycle ratio of the volume of liquid reactor effluent recycled back through the reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled, from about 1 to 1 to about 1000 to 1.

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68. The process according to claim 65, comprising a further step of feeding into a second reactor the portion of the liquid reactor effluent that is not recycled.

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69. The process according to claim 68, wherein the second reactor is provided with a solid hydrogenation catalyst and hydrogen gas.

70. The process according to claim 69, comprising a further step of recycling a portion of a liquid reactor effluent exiting the second reactor back through the second reactor, at a recycle ratio of the volume of the liquid reactor effluent recycled back through the second reactor, with respect to the volume of the portion of the liquid reactor effluent that is not recycled back through the second reactor, of at least about 1 to 1.

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71. The process according to claim 65, wherein the aldol catalyst solution comprises a solution of an alkali- or an alkaline- earth metal hydroxide or alkoxide, wherein the hydroxide or alkoxide is present in the solution in an amount of from about 0.5 to about 50 wt. %.

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72. The process according to claim 65, wherein the molar ratio of the hydroxide or alkoxide of the alkali metal or alkaline earth metal catalyst to acetaldehyde is from about 0.001:1 to about 0.4:1.

5 73. The process according to claim 65, wherein the aldol catalyst solution comprises one or more of: sodium hydroxide or potassium hydroxide.

10 74. The process according to claim 65, wherein the temperature in the reactor is from about 0°C to about 200°C.

75. The process according to claim 65, wherein the hydrogen gas is provided at a pressure from about 3 to about 150 bar.

15 76. The process according to claim 65, wherein the residence time of the reaction mixture in the reactor is from about 2 to about 200 minutes.

20 77. The process according to claim 65, where the hydrogenation catalyst is a shaped or extruded transition metal catalyst supported on a stable support.

25 78. The process according to claim 65, wherein the hydrogenation catalyst comprises one or more of: Ni, Co, Cu, Cr, Pt, Pd, Rh, Ru, Re, or Ir.

79. The process according to claim 65, wherein the hydrogenation catalyst is supported on a stable support comprising one or more of: alumina, silica, silica-alumina, or carbon.

- 5 80. The process according to claim 65, wherein the hydrogenation catalyst comprises palladium on carbon.